

# The Convergence Properties of Hindered Rotor Energy Levels.

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## Abstract

The Schrödinger equation describing one-dimensional hindered rotation of one *CHO* group against the other in glyoxal is solved variationally using three sets of basis functions and an experimentally derived potential taken from the literature. Reference states are defined by the free rotor potential, a single well potential and a double well potential. Of the basis sets studied, the double well reference states provide the most rapidly convergent reference functions for solving the full hindered rotor Hamiltonian. In the case of the free rotor and double well reference states, unusual patterns to convergence were observed for the *cis* levels.

## I. INTRODUCTION

Many organic molecules exhibit the ability to interconvert between isomers by internal rotation of functional groups about a chemical bond. This large amplitude ‘top versus frame’ motion [1] is one of  $3N - 6$  vibrational degrees of freedom and commonly called torsion or hindered rotation. As with all vibrational motions, hindered rotation is probed spectroscopically to derive information about the potential energy surface. Spectroscopic data can seldom be inverted directly to yield information about the atomic interactions, so a functional form with adjustable parameters is often assumed for the potential function. The potential surface is found acceptable when the transition frequencies calculated by solving the vibrational Schrödinger equation with the model potential match the spectroscopically determined frequencies.

One method of testing the model potential function against the spectroscopic data is to solve the Schrödinger equation variationally [2], [3]. In a variational calculation, the Hamiltonian operator is expressed in a truncated set of reference functions. The resulting matrix is then diagonalized, yielding the eigenvalues and eigenfunctions of the Hamiltonian. The eigenvalues are upper bounds to the eigenvalues of the infinite variational matrix [4]. The eigenfunctions are vectors linearly expanded on the reference functions.

The size of the variational matrix depends on the number of reference or basis functions required to attain converged eigenvalues, so computational effort is minimized by using the most rapidly convergent set of reference functions. In fact, a rapidly convergent basis set is often a requirement in a multi-dimensional variational problem. Since the variational matrix is usually constructed and diagonalized in memory, there is an upper limit on the basis size. While this has little effect on the one-dimensional problem, the restriction on matrix size can severely limit the number of converged levels obtainable in a multi-dimensional problem [5]. Finding a rapidly convergent set of reference functions for each degree of freedom in a multi-dimensional problem, therefore, can be critical to the success of the calculation. Furthermore, the ability to interpret the wavefunction depends on the convergence properties

of the basis set. In the one-dimensional problem, simple inspection of the eigenfunctions yields the approximate quantum numbers used by experimentalists. In a multi-dimensional problem, the assignments are made by citing the reference functions with the largest coefficients. This process is accurate only when each state is composed of a few dominant reference functions. Assignments quickly become impossible in a slowly convergent basis because then each state is composed of many reference functions of similar importance.

It is the aim of this work to find a rapidly convergent basis set for the one-dimensional hindered rotation variational problem applied to a specific organic molecule: glyoxal. Using a model potential function taken from the literature, we study the convergence properties of the torsional energy levels calculated in three different basis sets. While the work is done on a specific potential model in one dimension, we argue the results are useful in the context of a multi-dimensional variational problem and applicable to any general hindered rotor potential model. In the course of carrying out this work, we discovered some unexpected features in the convergence patterns for levels calculated in two of the three basis sets.

## II. MODEL POTENTIAL FUNCTION

Glyoxal,  $(CHO)_2$ , is the simplest  $\alpha - \beta$  dicarbonyl and possesses a low frequency torsion vibrational mode corresponding to rotation about the  $C - C$  bond. The potential associated with a change in the torsion coordinate is characterized by two non-equivalent minima, allowing the molecule to exist in either the *trans* or *cis* conformation. Many experimentalists have probed the potential surface including Butz, Krajnovich and Parmenter [6], who spectroscopically determined most of the energy levels supported by the *trans* portion of the potential as well as a level in the *cis* part of the potential.

Following the example of Lewis and coworkers [7], Butz and coworkers applied the variational method to solve the hindered rotor problem in one dimension using free rotor expansion functions and derived a torsional potential energy surface for glyoxal that matches the experimental data [6]. The periodic potential takes the familiar form of a cosine Fourier

series,

$$V = \frac{1}{2} \sum_{n=1}^6 V_n (1 - \cos n\tau) \quad (1)$$

with parameter values (in  $\text{cm}^{-1}$ )  $V_1 = 1719 \cdot 4$ ,  $V_2 = 1063 \cdot 5$ ,  $V_3 = -53 \cdot 2$ ,  $V_4 = -81 \cdot 9$ ,  $V_5 = 21 \cdot 3$  and  $V_6 = 2 \cdot 9$ . The potential used in the present calculations is defined by this equation.

### III. CALCULATION OF ENERGY LEVELS

The Hamiltonian operator for hindered rotation is constructed using the assumption that the torsion mode is uncoupled from all the other vibrational modes in the molecule. In addition, the Hamiltonian applies to the  $J=0$  rotational state, and coupling between internal and overall angular momentum of the molecule is neglected. The Hamiltonian for the fully coupled vibrational problem and methods for determining its eigenvalues using local mode calculations will be described in a subsequent publication [8].

Lewis, Malloy, Chao and Laane [7] reported the Hamiltonian for a potential written as a Fourier expansion:

$$\hat{H} = -\frac{d}{d\tau} B(\tau) \frac{d}{d\tau} + V(\tau) \quad (2)$$

where  $V(\tau)$  is the hindering potential defined by Equation 1 and  $B(\tau)$  is the internal rotation constant. This constant depends on the internal rotation coordinate,  $\tau$ , due to structural relaxation that occurs during motion along the torsion coordinate. It is known accurately only for the energetically stable *cis* ( $\tau = 180^\circ$ ) and *trans* ( $\tau = 0^\circ$ ) isomers [6]. To conform to the functional form of the potential function, the rotational constant is also written as a Fourier series expansion,

$$B = B_0 + \sum_{n=1}^5 B_n \cos n\tau \quad (3)$$

Durig, Bucy and Cole [9], in an earlier study of the glyoxal torsional surface, determined the set of coefficients for the internal rotation constant (in  $\text{cm}^{-1}$ ),  $B_0 = 4 \cdot 213$ ,  $B_1 = -1 \cdot 116$ ,

$B_2 = 0 \cdot 421$ ,  $B_3 = -0 \cdot 126$ ,  $B_4 = 0 \cdot 040$ , and  $B_5 = -0 \cdot 015$ . Butz *et al* [6] used these coefficients during the development of the torsional potential surface, Equation 1, and we use this form in the present study.

To determine the energy levels and wave functions of the Hamiltonian, Equation 2, the operator is written in matrix form using a set of basis functions  $\psi_k$  that span the space and satisfy the appropriate boundary conditions. The set is usually chosen to be the eigenfunctions obtained by analytically solving some component of the Hamiltonian, called the reference Hamiltonian. For vibrational problems such as the one considered here, this basis set is usually infinite and must be truncated at  $N$  functions. Expressing the full Hamiltonian in this truncated representation leads to an  $N \times N$  matrix with elements,

$$H_{j,k} = \int_0^{2\pi} \psi_j^* \hat{H} \psi_k d\tau \quad (4)$$

Diagonalization of the matrix yields the  $N$  eigenvalues,  $E_n$ , and the corresponding eigenfunctions

$$\phi_n = \sum_{k=0}^{N-1} C_{k,n} \psi_k \quad (5)$$

where  $n$  is the quantum number and the coefficients  $C_{k,n}$  are the elements of the transformation matrix.

If the basis functions possess symmetry properties, the variational matrix may be factorized into smaller sub-blocks, each belonging to a different symmetry class. Although the problem can be solved in basis functions possessing no particular symmetry properties, computational effort is reduced by taking advantage of symmetry. In the case of the free rotor reference functions, for example, using the cosine/sine forms of the functions to break the problem into even/odd symmetry blocks requires storing and diagonalizing two  $N \times N$  matrices rather than one  $2N \times 2N$  matrix constructed in the complex representation of free rotor solutions ( $e^{im\tau}$ ).

In the present study, the Hamiltonian operator is expressed in three different basis sets. Each basis set is obtained by analytically solving a component of the full Hamiltonian, the

reference Hamiltonian, which is composed of the same kinetic energy term,  $B_0 \frac{d^2}{d\tau^2}$ , plus a unique potential term. All expansion functions possess either even or odd parity.

Following the traditional method established by Lewis and coworkers [7], the first basis set,  $V_0$ , consists of the solutions to the free rotor problem. The reference potential  $V = 0$  and the reference eigenstates are:

$$\begin{aligned}\psi_0^{Even} &= \frac{1}{\sqrt{2\pi}} \\ \psi_n^{Even} &= \frac{1}{\sqrt{\pi}} \cos(n\tau) \quad n = 1, 2, 3\ldots \\ \psi_n^{Odd} &= \frac{1}{\sqrt{\pi}} \sin(n\tau) \quad n = 1, 2, 3\ldots\end{aligned}\tag{6}$$

The other two basis sets used in this study are solutions to Mathieu's differential equation [10]. Using the potential function,  $\frac{1}{2}V_n(1 - \cos n\tau)$ , and a change of variables,  $x = (n\tau + \pi)/2$ , the Schrödinger equation for internal rotation maps into Mathieu's equation [11]. Solutions come in two varieties of even/odd pairs; those periodic in  $\pi$  ( $T = \pi$ ) and those periodic in  $2\pi$  ( $T = 2\pi$ ). The solutions to Mathieu's equation are known analytically and may be calculated using computer code developed by Shirts [12].

The second basis set,  $V_1$ , is obtained by solving Mathieu's equation for the single well reference potential defined by the first term in the full potential in Equation 1,  $\frac{1}{2}V_1(1 - \cos \tau)$ . In terms of the variable  $x = (\tau + \pi)/2$  and using subscripts to indicate those solutions with the correct boundary conditions (periodic in  $\pi$ ), the reference eigenstates are:

$$\begin{aligned}\psi_{2n}^{Even} &= \frac{1}{\sqrt{\pi}} \left( 2 \sum_{k=1}^{\infty} c_k \cos 2kx + c_0 \right) \quad n = 0, 1, 2\ldots \\ \psi_{2n+2}^{Odd} &= \frac{1}{\sqrt{\pi}} \left( 2 \sum_{k=1}^{\infty} c_k \sin 2kx \right) \quad n = 0, 1, 2\ldots\end{aligned}\tag{7}$$

The third basis set,  $V_2$ , is determined by solving Mathieu's equation for the reference potential defined by the second term of the full potential in Equation 1,  $\frac{1}{2}V_2(1 - \cos 2\tau)$ . A change of variables is not required because Mathieu's equation is defined for this potential. Both varieties of solution conform to the correct boundary conditions (periodic in  $2\pi$ ),

$$\begin{aligned}
\psi_{2n}^{Even} &= \frac{1}{\sqrt{2\pi}} \left( 2 \sum_{k=1}^{\infty} c_k \cos 2k\tau + c_0 \right) & n = 0, 1, 2, \dots & \quad T = \pi \\
\psi_{2n+1}^{Odd} &= \frac{1}{\sqrt{2\pi}} \left( 2 \sum_{k=0}^{\infty} c_k \sin (2k+1)\tau \right) & n = 0, 1, 2, \dots & \quad T = 2\pi \\
\psi_{2n+1}^{Even} &= \frac{1}{\sqrt{2\pi}} \left( 2 \sum_{k=0}^{\infty} c_k \cos (2k+1)\tau \right) & n = 0, 1, 2, \dots & \quad T = 2\pi \\
\psi_{2n+2}^{Odd} &= \frac{1}{\sqrt{2\pi}} \left( 2 \sum_{k=1}^{\infty} c_k \sin 2k\tau \right) & n = 0, 1, 2, \dots & \quad T = \pi
\end{aligned} \tag{8}$$

The convergence properties of the eigenenergies of the Hamiltonian, expressed in each basis set, are studied by varying the number of functions used in the expansion. For the purpose of this paper, we assume an energy level is converged when the addition of more basis functions to the truncated set causes less than a  $0.01 \text{ cm}^{-1}$  change in energy. The accuracy of the calculation is confirmed by noting that the levels should converge to the same value, regardless of which set of reference functions is used. The states labelled *trans* have greater amplitude over the deeper minimum in the potential well. Similarly, *cis* states have greater amplitude over the shallower potential minimum. Solutions with an equal distribution of amplitude over the full range of torsion coordinate are labelled *free*. The state is labelled *even* if  $\phi(\tau) = \phi(-\tau)$  and *odd* if  $\phi(\tau) = -\phi(-\tau)$ .

We expect basis sets obtained by solving Mathieu's equation ( $V_1$  or  $V_2$ ) to converge the energy levels in fewer terms than the free rotor basis, at least for lower quantum numbers, because these reference potentials include a component of the full torsional potential (see Figure 1).

#### IV. RESULTS AND DISCUSSION

Table I shows the results of converging the hindered rotation energy levels of glyoxal to within  $0.01 \text{ cm}^{-1}$ . With the exception of the first few *cis* states, which will be discussed separately, the levels up to  $n=40$  quanta calculated in the Mathieu representations  $V_1$  and  $V_2$  converge in a smaller basis set than those calculated in the free rotor representation, as expected. The  $V_1$  single well reference potential and the  $V_2$  double well reference potential

yield converged energy levels in approximately the same number of basis terms. The lowest energy levels converge in Mathieu basis sets in less than half the number of terms required by the free rotor basis. In particular, it requires only 5 and 6 terms to converge the ground state energy in the  $V_1$  and  $V_2$  basis sets, respectively, compared to 15 terms in the free rotor basis. Higher energy levels converge several basis terms earlier in the Mathieu representations. High above the potential barrier, energy levels converge in essentially the same number of terms for all three basis sets. We anticipate this last result since the doubly degenerate free rotor functions are the solutions to the full hindered rotor problem and the Mathieu problems in this high energy region.

Table II illustrates the patterns of convergence for the  $n=0$  *trans* ground state level, the  $n=8$  *trans* excited level, and the  $n=15$  *cis* ground state level. In all basis sets, the zero-point level follows the usual pattern as guaranteed by Macdonald's theorem [4]: as the basis size increases, the  $n$ th eigenvalue decreases in value. In the  $V_1$  single well expansion functions, all energy levels converge following the same unremarkable pattern and more or less in sequence (see Table I). The *trans* ground state converges first and the higher states follow.

The first significant departure from the normal convergence pattern occurs for the  $n=8$  eigenvalue calculated in free rotor and double well basis functions. Eigenvalues printed in boldface type in Table II draw attention to the unusual pattern. The energy level appears to converge first to the wrong value,  $E = 1731 \cdot 28 \text{ cm}^{-1}$  in 8 free rotor functions, for instance, and then to converge many basis functions later to the correct value,  $E = 1035 \cdot 41 \text{ cm}^{-1}$  in 25 free rotor functions. Inspection of the 'wrong' solution, plotted in the top of Figure 2, reveals the  $n=8$  eigenstate is not the eighth excited *trans* state as expected, but rather the converged  $n=15$  *cis* ground state. In the free rotor basis set, the *cis* ground state level converges more rapidly than any other level, including the zero-point level. As the more slowly convergent levels drop down in value, the *cis* ground state level is pushed up the list of eigenvalues until it reaches its final position at  $n=15$ .

All the *cis* levels lying below the potential barrier and calculated in the free rotor and double well basis sets exhibit this unusual convergence pattern, but with an additional feature.



Within 10 basis functions, the states closely resemble their fully converged counterparts, but as the states change position in the list of eigenvalues, the energy fluctuates randomly about the converged value. For the first excited *cis* level, these fluctuations are smaller than the convergence criterion. The second excited state fluctuations occur on the order of wavenumbers and the third excited state fluctuations are tens of wavenumbers. Although these fluctuations make it impossible to determine convergence with the usual test, in no way do they violate Macdonald’s theorem [4], which applies to eigenvalues identified only by their order. Once a level assumes its final position in the list of eigenvalues, its energy converges in the conventional pattern. We are unaware of previous reports of this unusual convergence pattern in the case of a one-dimensional variational problem. Similar effects have been observed in a fully coupled six-dimensional variational calculation carried out by Bramley and Handy in 1992 [5].

Referring to the plot of the reference potentials in Figure 1, it is apparent why the *cis* levels should converge rapidly in the free rotor and double well basis sets but not in the single well basis set. It is easy to predict that only the  $V_1$  reference states lying above the single well potential would have sufficient amplitude in the  $\tau = \pi$  region to describe a localized *cis* state. Similarly, it is apparent from a plot of the double well potential that a combination of low-lying  $V_2$  reference states is able to describe a localized *cis* state. Low energy free rotor reference functions (Equation 6) and double well reference functions (Equation 8) have significant amplitude over the *cis* portion of the potential well, whereas the low energy single well reference functions (Equation 7) have negligible amplitude in that region. For this reason, both the single well and double well reference functions converge the *trans* states equally well, but the free rotor and double well reference functions converge the *cis* states much better than the single well functions. Considering all the energy levels, the double well potential function provides the most rapidly convergent set of reference functions.

The eigenfunctions of the hindered rotor Hamiltonian fall into even or odd symmetry classifications in any basis set, regardless of the symmetry characteristics of the expansion functions. As shown in Table I, the eigenfunctions labelled *trans* alternate even and odd in

parity. Similarly, the *cis* eigenfunctions also alternate in parity. In contrast, neighboring eigenfunctions do not simply alternate in parity. The pattern is broken when the even ground state *cis* function (n=15) converges just above (in energy) an even *trans* state. The symmetry pattern changes with the introduction of the *cis* state to an even/odd odd/even sequence. Within each pair of *cis/trans* solutions, as illustrated in Figure 3, one function is even and the other odd.

An analysis of the symmetry along with the shape of the eigenstates provides enough information to predict the spectroscopically allowed transitions [11]. Transitions cannot occur from a *trans* to a *cis* state if the eigenfunctions are localized. The dotted lines in Figure 4 indicate localized eigenfunctions exist up to quantum number n=23, just below the barrier. Also, transitions cannot occur between states of the same symmetry. Thus, in theory, glyoxal cannot absorb radiation to make a change from one rotational isomer to the other when it occupies states in either conformation lower than n=23.

For the one-dimensional problem discussed here, it is assumed the torsion is independent of the remaining  $3N - 7$  vibrational modes of the molecule. In reality, the torsional mode interacts with other vibrational degrees of freedom and these interactions are included in the Hamiltonian of the fully coupled multi-dimensional problem. It is reasonable to express the wave function for the coupled problem in a basis composed of a sum of products of single variable vibrational functions provided matrix elements of the correction Hamiltonian are small and Fermi resonances unimportant.

In the specific case of glyoxal, we anticipate that matrix elements of the correction Hamiltonian coupling torsion to other vibrational modes will be small and Fermi resonances between torsion and any other mode unimportant. The fact that a one-dimensional torsion potential model, such as Equation 1, reproduces the experimentally determined torsional frequencies to high accuracy suggests that coupling of the torsional mode to other vibrational modes is small. Furthermore, calculations done by R. Meyer [1] indicate the torsion interacts with the  $\nu_{12}$  CCO antisymmetric skeletal bending mode through Coriolis coupling in the kinetic energy operator. Meyer found that adding the Coriolis coupling terms altered the

torsional and CCO bending transition frequencies by only a few per cent, but significantly improved the agreement to the measured rotational frequencies. According to perturbation theory, Coriolis forces are responsible for second-order perturbations between vibrations in the absence of Fermi resonance [13]. Thus, in the particular case of glyoxal, a set of Mathieu functions in the torsion coordinate should provide a suitable representation in the fully coupled problem. For molecules in which the torsional coupling terms are small but Fermi resonances are important, a basis composed of the natural orbital functions [14] may be more appropriate.

## V. CONCLUSION

We have compared the convergence properties of hindered rotor energy levels calculated in three different sets of basis functions. Following the example of Lewis, Malloy, Chao and Laane [7], we constructed the Hamiltonian operator for hindered rotation using a potential energy function taken from the literature and then solved the Schrödinger equation variationally in a set of expansion functions defined by the free rotor potential function. With the aid of Shirts’ computer code [12], we modified the method and solved the same problem twice more, this time mapping it onto Mathieu’s differential equation. The first term in the potential function defined the single well reference potential and the second term defined the double well reference potential for the Mathieu problems.

Of the three basis sets studied, energy levels converged fastest in the double well reference functions. The rapidly convergent *cis* levels in both the free rotor and double well basis sets changed position in the order of eigenvalues as lower levels converged at slower rates. A similar convergence pattern with regard to a multi-dimensional problem has been observed in an earlier study by Bramley and Handy [5].

The best reference functions cause the energy levels to converge rapidly to a specified accuracy. For the torsional degree of freedom and the model potential function studied here, we found the best reference functions of those studied arose from solving Mathieu’s

differential equation for a double well potential. In any general hindered rotation problem, a set of Mathieu reference functions should always outperform the free rotor functions because the reference Hamiltonian contains some portion of the full potential. In the context of a multi-dimensional variational problem in which the coupling terms in the Hamiltonian are small and Fermi resonances unimportant, using the most rapidly convergent basis set in each degree of freedom is essential to obtaining converged eigenvalues and assigning quantum numbers.

## VI. ACKNOWLEDGMENTS

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# FIGURES

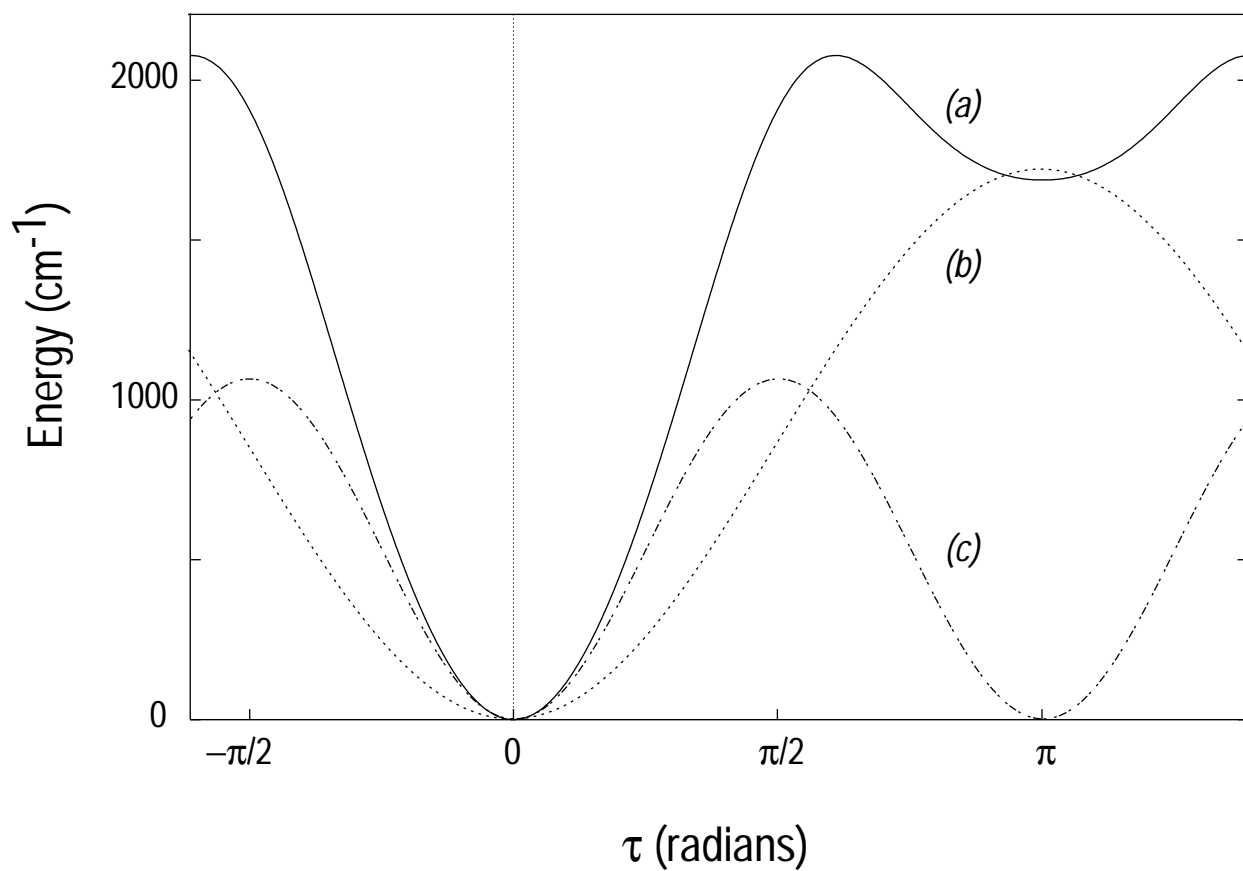


FIG. 1. Potential energy plotted as a function of the torsion coordinate. (a). The full torsional potential energy surface defined by Equation 1. (b). The single well reference potential energy surface. (c). The double well reference potential energy surface.  $V=0$  for the free rotor reference potential energy surface.

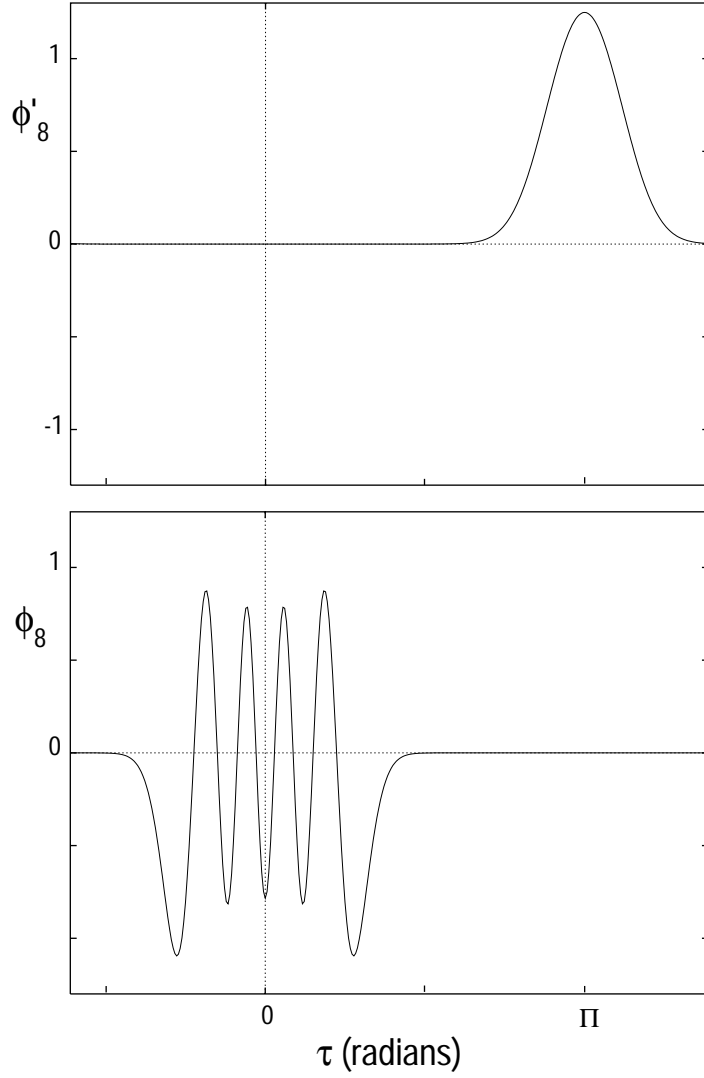


FIG. 2. The  $n=8$  solution to the hindered rotor problem as defined by the Hamiltonian in Equation 1 plotted as a function of the torsion coordinate. Results are given for the double well ( $V_2$ ) basis set with  $N=8$  and  $N=20$  members. The upper plot shows that the solution obtained using 8 double well reference functions is the converged  $n=15$  ground state *cis* function,  $E_8 = 1731 \cdot 28 \text{ cm}^{-1}$ . The lower plot shows the ‘true’  $n=8$  solution, converged using 20 double well functions,  $E_8 = 1035 \cdot 39 \text{ cm}^{-1}$ . Similar wavefunctions are obtained using  $N=9$  and  $N=25$  free rotor functions.

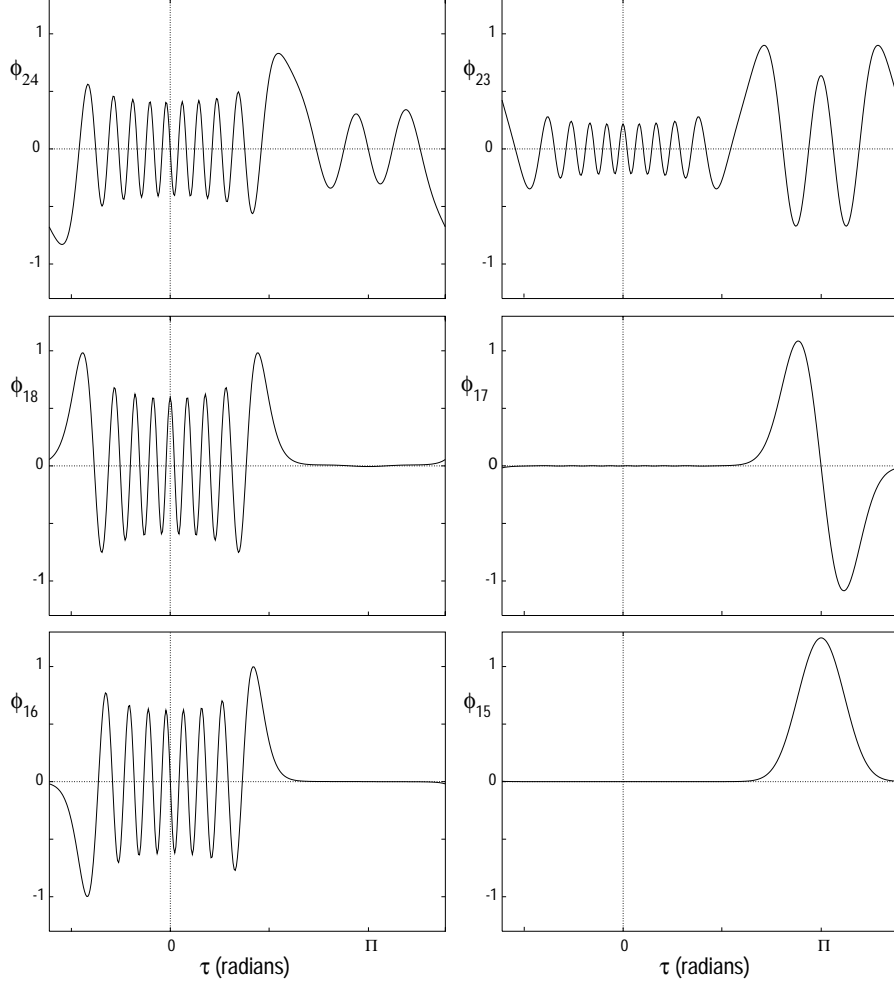


FIG. 3. Pairs of solutions to the Schrödinger equation defined by the Hamiltonian in Equation 2 plotted as a function of the torsion coordinate. The *trans* solutions are arranged in the left column and the *cis* solutions in the right column. Each member of the *trans/cis* pair (shown as a row) possesses different parity. The solutions begin sharing amplitude over both minima of the potential surface beginning with the  $n=23$  and  $n=24$  pair. With increasing quantum number, the pairs gradually lose *trans/cis* character and separation in energy. At very high quantum numbers, the solutions are the doubly degenerate free rotor functions.



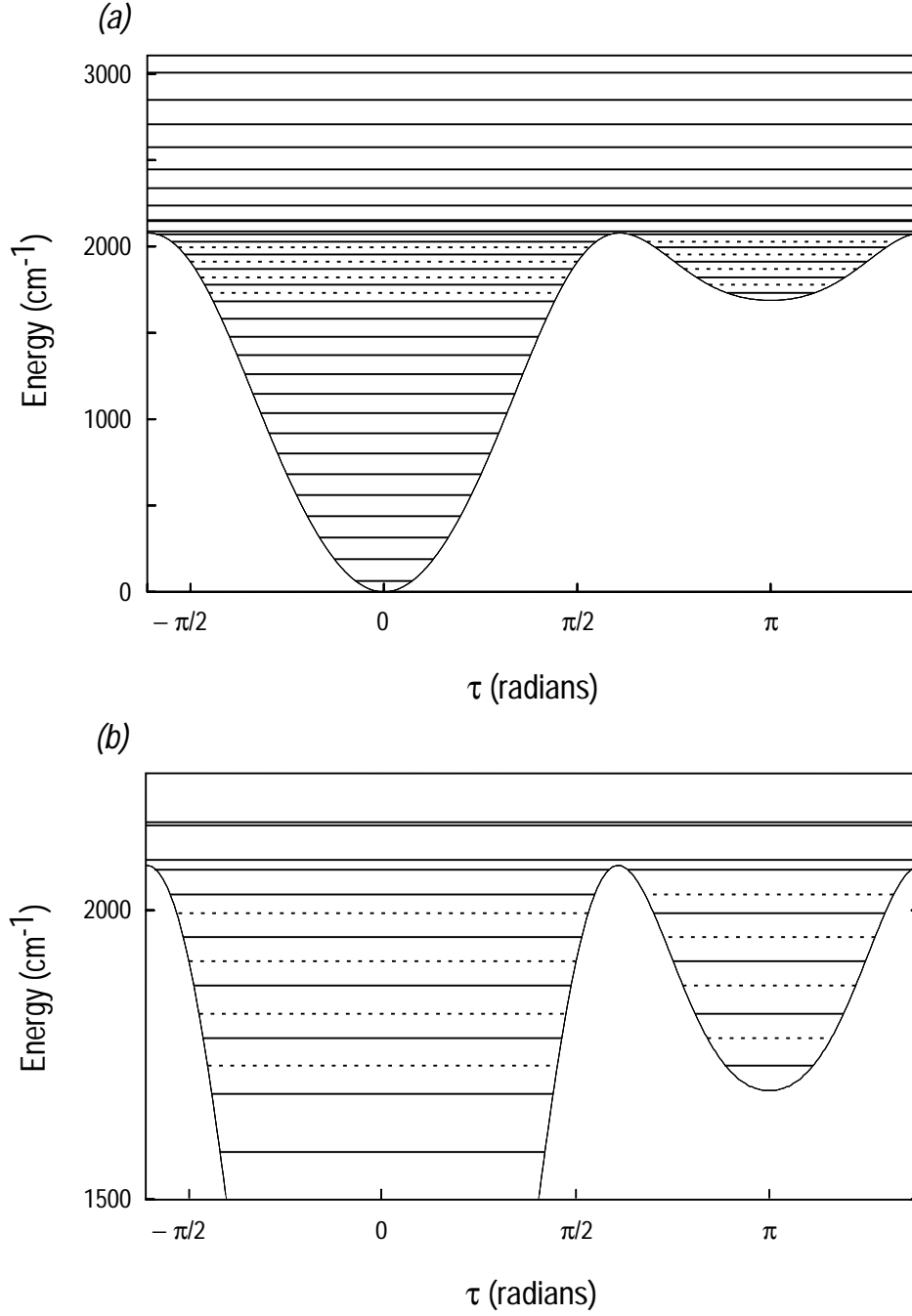


FIG. 4. In (a) the full torsional potential energy surface of Equation 1 is plotted as a function of the torsion coordinate with the energy levels inscribed by horizontal lines. Dotted lines signify an eigenstate with negligible amplitude in that region of the potential energy surface. In (b) the same function is plotted with the energy region between 1500 and 2250  $\text{cm}^{-1}$  enlarged.

# TABLES

TABLE I. Converged energies and number of expansion functions required in each basis set.

n	$E_n(cm^{-1})$	$V_0$	$V_1$	$V_2$	Symmetry	Isomer
0	63.83	15	5	6	even	<i>trans</i>
1	190.55	16	6	6	odd	<i>trans</i>
2	315.73	18	8	10	even	<i>trans</i>
3	439.43	19	10	11	odd	<i>trans</i>
4	561.68	21	12	14	even	<i>trans</i>
5	682.48	21	14	15	odd	<i>trans</i>
6	801.76	23	16	17	even	<i>trans</i>
7	919.44	23	17	18	odd	<i>trans</i>
8	1035.39	25	19	20	even	<i>trans</i>
9	1149.46	25	19	20	odd	<i>trans</i>
10	1261.43	27	21	22	even	<i>trans</i>
11	1371.08	26	21	21	odd	<i>trans</i>
12	1478.09	28	23	23	even	<i>trans</i>
13	1582.08	28	23	23	odd	<i>trans</i>
14	1682.60	29	25	25	even	<i>trans</i>
15	1731.28	9	18	8	even	<i>cis</i>
16	1778.97	29	24	24	odd	<i>trans</i>
17	1822.13	9	17	8	odd	<i>cis</i>
18	1870.30	30	26	26	even	<i>trans</i>
19	1911.90	25	19	22	even	<i>cis</i>
20	1954.91	30	25	25	odd	<i>trans</i>
21	1995.46	27	22	24	odd	<i>cis</i>
22	2028.59	31	27	27	even	<i>trans</i>
23	2070.36	30	26	26	even	<i>cis</i>
24	2088.53	30	26	26	odd	<i>trans</i>
25	2148.15	30	26	26	odd	<i>cis</i>
26	2153.73	32	27	27	even	<i>trans</i>
27	2237.69	32	28	28	even	<i>cis</i>
28	2238.61	31	27	27	odd	<i>trans</i>
29	2339.17	32	28	28	odd	free
30	2339.27	33	29	29	even	free
31	2452.00	33	29	29	even	free
32	2452.00	33	29	29	odd	free
33	2575.44	33	29	29	odd	free
34	2575.44	34	30	30	even	free
35	2708.93	34	30	30	even	free

36	2708·93	35	31	31	odd	free
37	2852·08	35	31	31	odd	free
38	2852·08	36	32	32	even	free
39	3004·61	35	32	31	even	free
40	3004·61	36	33	32	odd	free

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TABLE II. Calculated energy levels for  $n=0$ ,  $n=8$ , and  $n=15$  as a function of basis set size,  $N_{basis}$ . The basis sets are factorized into odd and even sub-sets, so that the state  $E_8$  first appears with a set of 5 even states and  $E_{15}$  with a set of 8 odd states.

$N_{basis}$	$E_0$			$E_8$			$E_{15}$		
	$V_0$	$V_1$	$V_2$	$V_0$	$V_1$	$V_2$	$V_0$	$V_1$	$V_2$
1	1336.00	76.06	903.65						
2	583.22	65.36	64.91						
3	291.93	64.03	64.79						
4	176.48	63.86	63.85						
5	122.26	63.83	63.84	2002.83	1348.92	1975.90			
6	94.24		63.83	1943.41	1203.48	1918.03			
7	79.20			1861.76	1125.70	1731.31			
8	71.19			1731.35	1082.55	<b>1731.28</b>	2145.52	2065.21	2495.94
9	67.10			<b>1731.28</b>	1059.11	<b>1731.28</b>	2140.98	2031.74	2178.77
10	65.16			<b>1731.28</b>	1046.94	1201.31	2089.97	1968.60	2118.10
11	64.32			1629.65	1040.95	1168.42	2027.64	1926.85	1995.87
12	63.99			1487.48	1038.13	1109.68	1995.55	1888.17	1995.04
13	63.88			1366.63	1036.94	1075.92	1994.99	1854.09	1951.76
14	63.84			1268.22	1036.36	1054.03	1967.74	1773.24	1855.96
15	63.83			1191.01	1035.86	1042.53	1911.90	1739.51	<b>1822.13</b>
16				1132.94	1035.58	1037.57	1848.87	1731.68	<b>1822.13</b>
17				1091.65	1035.46	1035.90	<b>1822.13</b>	1731.30	<b>1822.13</b>
18				1064.55	1035.41	1035.48	<b>1822.13</b>	1731.28	1766.41
19				1048.64	1035.39	1035.40	<b>1822.13</b>		1731.28
20				1040.56		1035.39	1794.81		
21				1037.11			1753.03		
22				1035.88			1731.28		
23				1035.51					
24				1035.41					
25				1035.39					